

Recently Detected Drinking Water Contaminants: GenX and Other Per- and Polyfluoroalkyl Ether Acids

ZACHARY R. HOPKINS,¹ MEI SUN,² JAMIE C. DEWITT,³ AND DETLEF R.U. KNAPPE¹

¹Department of Civil, Construction, and Environmental Engineering, North Carolina State University, Raleigh, N.C.

²Department of Civil and Environmental Engineering, University of North Carolina at Charlotte, Charlotte, N.C.

³Department of Pharmacology and Toxicology, East Carolina University, Greenville, N.C.

For several decades, a common processing aid in the production of fluoropolymers was the ammonium salt of perfluorooctanoic acid (PFOA). Because PFOA is persistent, bioaccumulative, and toxic, its production and use are being phased out in the United States. In 2009, the US Environmental Protection Agency stipulated conditions for the manufacture and commercial use of GenX, a PFOA replacement. While GenX is produced for commercial purposes, the acid form of GenX is also generated as a byproduct during the production of fluoromonomers. The discovery of high concentrations

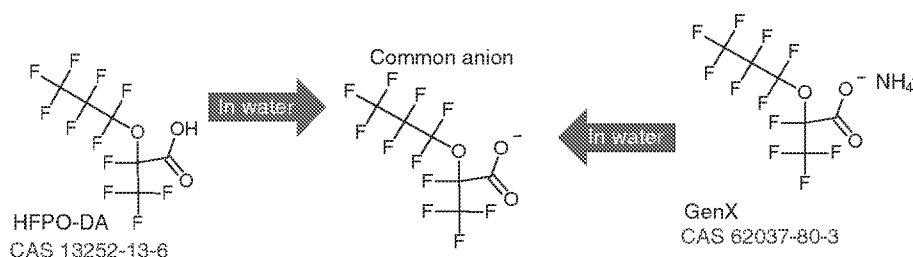
of GenX and related perfluoroalkyl ether acids (PFEAs) in the Cape Fear River and in finished drinking water of more than 200,000 North Carolina residents required quick action by researchers, regulators, public health officials, commercial laboratories, drinking water providers, and consulting engineers. Information about sources and toxicity of GenX as well as an analytical method for the detection of GenX and eight related PFEAs is presented. GenX/PFEA occurrence in water and GenX/PFEA removal by different drinking water treatment processes are also discussed.

Keywords: *emerging per- and polyfluoroalkyl substances, hexafluoropropylene oxide dimer acid (HFPO-DA), Nafion by-products, industrial wastewater, unregulated contaminants*

The presence of per- and polyfluoroalkyl substances (PFASs) in drinking water sources and finished drinking water is receiving increased attention by water treatment professionals and regulators. Factors that have contributed to the raised awareness include the US Environmental Protection Agency's (USEPA's) announcement of a 70 ng/L health advisory level (HAL) for the sum concentration of perfluorooctane sulfonic acid (PFOS) (USEPA 2016a) and perfluorooctanoic acid (PFOA) (USEPA 2016b), analysis of USEPA's third Unregulated Contaminant Monitoring Rule (UCMR 3) data showing that more than six million US residents consume drinking water with combined PFOA and PFOS levels above the 70 ng/L HAL (Hu et al. 2016), and state-level efforts to introduce drinking water standards for PFASs, such as the recently recommended maximum contaminant levels for PFOA (14 ng/L; NJ DEP 2017) and perfluorononanoic acid (13 ng/L; NJ DEP 2015) in New Jersey. Also, extensive media coverage has been dedicated to the contamination of public drinking water wells with PFOA, PFOS, and other

PFASs at numerous locations, including the Parkersburg, W.Va., region; Cottage Grove, Minn.; Hoosick Falls, N.Y.; Bennington, Vt.; Merrimack, N.H.; Plainfield Township, Mich.; and Fountain, Colo. In North Carolina, high levels of emerging PFASs, such as GenX, were first reported in Cape Fear River water (Strynar et al. 2015) and later in finished drinking water of more than 200,000 North Carolina residents (Sun et al. 2016). Peer-reviewed papers (Sun et al. 2016, Strynar et al. 2015), as well as an article in *The Intercept* (Lerner 2016), did not initially raise concerns about GenX in the lower Cape Fear River basin. It was not until June 8, 2017, when an article was published in the *Wilmington Star News* (Hagerty 2017), that residents, local officials, and state regulators became fully aware of the extent of the water contamination. The objective of this article is to summarize available information about GenX and other perfluoroalkyl ether acids (PFEAs) in a context relevant to drinking water providers. This article is divided into five parts: (1) sources of GenX and other PFEAs, (2) toxicity of

FIGURE 1 Structures of HFPO-DA and GenX as well as the common carboxylate anion that forms in water



CAS—Chemical Abstracts Service, HFPO-DA—hexafluoropropylene oxide-dimer acid

GenX and development of North Carolina's health goal, (3) analytical methods for GenX and other PFEAs, (4) occurrence, and (5) treatment options. Information from the literature is amalgamated with results from ongoing research in the authors' laboratories, at USEPA, and at affected utilities.

GENX AND RELATED COMPOUNDS—BACKGROUND AND SOURCES

GenX (Figure 1) is the trade name for the ammonium salt of hexafluoropropylene oxide-dimer acid (HFPO-DA). GenX serves as a replacement for ammonium perfluorooctanoate, the ammonium salt of PFOA, and it is used as a processing aid in the production of fluoropolymers such as polytetrafluoroethylene (PTFE). As shown in Figure 1, GenX and HFPO-DA form the same anion when dissolved in water—in the case of GenX, the

ammonium group leaves, and in the case of HFPO-DA, which is a relatively strong acid (Table 1), the proton of the carboxylic acid functional group leaves. Discussing GenX/HFPO-DA can be challenging because a number of different terms have been used by the manufacturer and regulators to describe GenX and HFPO-DA (Table 1). From a water quality and treatment perspective, GenX and HFPO-DA discharges lead to the same anionic species (Figure 1) that would have to be removed from water; therefore, for the purposes of this article, GenX generically refers to the common anion shown in Figure 1. Conditions for the production and use of GenX and HFPO-DA were stipulated in a 2009 consent order (USEPA 2009a). The consent order requires 99% capture of GenX in wastewater discharges and air emissions by GenX production facilities as well as by any customers using GenX.

TABLE 1 GenX and HFPO-DA nomenclature and properties

	GenX	HFPO-DA
CAS no.	62037-80-3	13252-13-6
IUPAC name	Azanium; 2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoate	2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid
Alternative names	C3-dimer salt, FRD-902, P-08-508 (USEPA 2009a), ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate	C3-dimer (acid), FRD-903, P-08-509 (USEPA 2009a), 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoic acid, perfluoro-2-methyl-3-oxahexanoic acid, perfluoro-2-propoxypropionic acid
Formula	C ₆ H ₄ F ₁₁ NO ₃	C ₆ HF ₁₁ O ₃
Formula weight—g/mol	347	330
pK _a	3.82 (Beekman et al. 2016), -0.77 ^b	-0.77 ^a
log K _{ow}	4.0 ^a	4.0 ^a , 3.21 ^b , 3.6 ^b , 8.12 ^d
log D (pH 7)	0.47 ^a	0.47 ^a , 1.34 ^d

CAS—Chemical Abstracts Service, HFPO-DA—hexafluoropropylene oxide-dimer acid, IUPAC—International Union of Pure and Applied Chemistry, USEPA—US Environmental Protection Agency

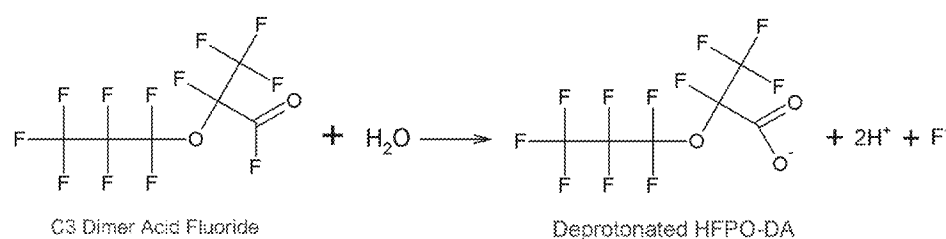
^aChemicalize, ChemAxon, Cambridge, Mass.

^bOPERA, CompTox Chemistry Dashboard, US Environmental Protection Agency (USEPA)

^cKOAWIN v1.10, EPI Suite, USEPA

^dPhysChem Module, Percepta, ACD/Labs, Toronto, Ont., Canada

FIGURE 2 Production of deprotonated HFPO-DA from C3 dimer acid fluoride



HFPO-DA—hexafluoropropylene oxide—dimer acid

One US facility where GenX is manufactured is located on the banks of the Cape Fear River near Fayetteville, N.C. Consistent with the 2009 consent order, the facility's National Pollutant Discharge Elimination System (NPDES) permit renewal application (The Chemours Company 2016) states that all wastewater from the polymer processing aid area of the plant where GenX is manufactured is captured and shipped off site for disposal. It was therefore surprising when Strynar et al. (2015) identified GenX downstream of the facility's wastewater discharge, and Sun et al. (2016) measured GenX concentrations up to approximately 4,500 ng/L at a drinking water intake located about 90 mi downriver. In a meeting with local officials in Wilmington, N.C., on June 15, 2017, the company stated that GenX is generated as a byproduct in its fluoromonomer production area and that GenX had been released through its wastewater treatment plant into the Cape Fear River since 1980 (Wagner & Buckland 2017). It is important to note that requirements of the USEPA consent order (USEPA 2009a), including the 99% capture stipulation, do not apply when GenX and/or HFPO-DA are generated as byproducts without separate commercial intent.

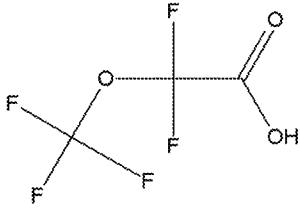
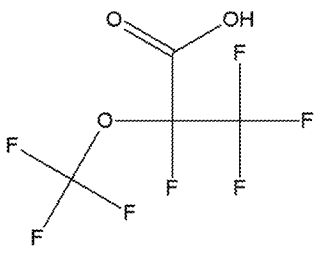
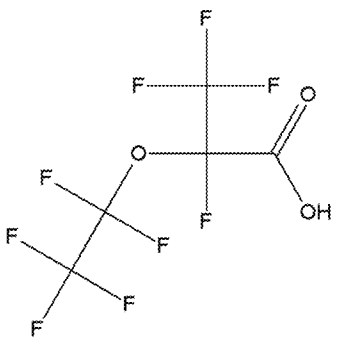
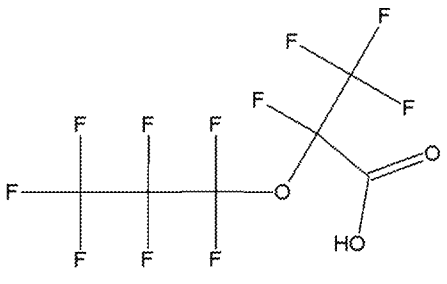
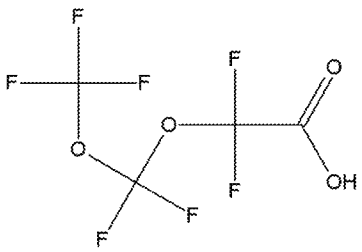
GenX discharges into surface water likely occur at other locations in the United States. For example, the West Virginia Department of Environmental Protection (WV DEP) permitted the discharge of GenX from two outfalls into the Ohio River with the requirement that, after mixing, the GenX concentration in the river does not exceed 17,500 ng/L (WV DEP 2011). According to documents submitted by the manufacturer to the WV DEP, GenX concentration limits that were set for the outfalls have been exceeded on several occasions (Bilott 2017).

In North Carolina, high levels of GenX (up to 4,000 ng/L) were also detected in private drinking water wells and in spring-fed lakes surrounding the manufacturing plant (NC DEQ 2018a, 2017b). Contamination of private wells located upgradient from the fluorochemical manufacturer strongly suggests that

air emissions of GenX and/or GenX precursors were followed by wet and/or dry deposition and subsequent percolation into the surficial aquifer. Air emissions were also implicated in the PFAS contamination of drinking water wells at other locations, such as in the Parkersburg, W.Va., region (Davis et al. 2007). A likely airborne precursor to GenX is the C3 dimer acid fluoride (Figure 2), which readily hydrolyzes to form deprotonated HFPO-DA when it comes into contact with water (Oppenheimer et al. 2007). Process models indicate that the fluorochemical manufacturing facility near Fayetteville, N.C., emitted 500–670 lb of C3 dimer acid fluoride annually into the air between 2012 and 2016 (NC DEQ 2017b) although the actual emissions may be substantially higher (NC DEQ 2018b). Air emissions of GenX and/or GenX precursors are likely sources of water contamination at other locations across the United States. For example, Lindstrom et al. (2017) found GenX in disconnected bodies of surface water in the Parkersburg, W.Va., region at distances of up to 20 mi from a fluorochemical manufacturing plant, where GenX is used to produce PTFE.

Apart from GenX, several other PFEAs (Table 2) have been detected both in the Cape Fear River and in finished drinking water downstream of the North Carolina fluorochemical manufacturing facility (Sun et al. 2016, Strynar et al. 2015). The identified compounds fall into three PFEA classes (Wang et al. 2017, Sun et al. 2016, Strynar et al. 2015): (1) mono-ether carboxylic acids with three to six carbon atoms, (2) multi-ether carboxylic acids with up to four ether oxygen atoms, and (3) multi-ether sulfonic acids. The compounds shown in Table 2 are thought to be byproducts emanating from the fluoromonomer and Nafion membrane production areas of the manufacturing facility. A subset of the compounds also has been detected in private well water (NC DEQ 2018c), suggesting that acid fluoride analogs of the compounds shown in Table 2 are released into air and that subsequent hydrolysis reactions lead to the formation of the acids shown in Table 2. Until recently, native and mass-labeled

TABLE 2 Perfluoroalkyl ether acids detected in Cape Fear River water and in finished drinking water

<p>Mono-ether carboxylic acids</p>    	<p>Compound</p> <p>Perfluoro-2-methoxyacetic acid (PFMOAA)</p> <p>Formula $C_3HF_5O_3$</p> <p>Molecular weight 180.0</p> <p>CAS no. 674-13-5</p> <p>Compound</p> <p>Perfluoro-2-methoxypropanoic acid (PFMOPrA)^a</p> <p>Formula $C_4HF_7O_3$</p> <p>Molecular weight 230.0</p> <p>CAS no. 13140-29-9</p> <p>Compound</p> <p>Perfluoro-2-ethoxypropanoic acid (PFEOPrA)^b</p> <p>Formula $C_5HF_9O_3$</p> <p>Molecular weight 280.0</p> <p>CAS no. NA</p> <p>Compound</p> <p>HFPO-DA (GenX), perfluoro-2-propoxypropanoic acid (PFPrOPrA)</p> <p>Formula $C_6HF_{11}O_3$</p> <p>Molecular weight 330.1</p> <p>CAS no. 13252-13-6</p>	<p>Perfluoro-2-methoxyacetic acid (PFMOAA)</p> <p>$C_3HF_5O_3$</p> <p>180.0</p> <p>674-13-5</p> <p>Perfluoro-2-methoxypropanoic acid (PFMOPrA)^a</p> <p>$C_4HF_7O_3$</p> <p>230.0</p> <p>13140-29-9</p> <p>Perfluoro-2-ethoxypropanoic acid (PFEOPrA)^b</p> <p>$C_5HF_9O_3$</p> <p>280.0</p> <p>NA</p> <p>HFPO-DA (GenX), perfluoro-2-propoxypropanoic acid (PFPrOPrA)</p> <p>$C_6HF_{11}O_3$</p> <p>330.1</p> <p>13252-13-6</p>
<p>Multi-ether carboxylic acids</p> 	<p>Compound</p> <p>Perfluoro-3,5-dioxahexanoic acid (PFO2HxA)</p> <p>Formula $C_4HF_7O_4$</p> <p>Molecular weight 246.0</p> <p>CAS no. 39492-88-1</p>	<p>Perfluoro-3,5-dioxahexanoic acid (PFO2HxA)</p> <p>$C_4HF_7O_4$</p> <p>246.0</p> <p>39492-88-1</p>

(Continued)

TABLE 2 Perfluoroalkyl ether acids detected in Cape Fear River water and in finished drinking water (*Continued*)

	<p>Compound</p> <p>Formula</p> <p>Molecular weight</p> <p>CAS no.</p>	<p>Perfluoro-3,5,7-trioxaoctanoic acid (PFO3OA)</p> <p>C₅HF₉O₅</p> <p>312.0</p> <p>39492-89-2</p>
	<p>Compound</p> <p>Formula</p> <p>Molecular weight</p> <p>CAS no.</p>	<p>Perfluoro-3,5,7,9-tetraoxadecanoic acid (PFO4DA)</p> <p>C₆HF₁₁O₆</p> <p>378.1</p> <p>39492-90-5</p>
<p>Multi-ether sulfonic acids</p>	<p>Compound</p> <p>Formula</p> <p>Molecular weight</p> <p>CAS no.</p>	<p>Ethanesulfonic acid, 2-[1-[difluoro(1,2,2-trifluoroethenyl)oxy]methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoro- (Nafion by-product 1)</p> <p>C₇HF₁₃O₅S</p> <p>443.9</p> <p>29311-67-9</p>
	<p>Compound</p> <p>Formula</p> <p>Molecular weight</p> <p>CAS no.</p>	<p>Ethanesulfonic acid, 2-[1-[difluoro(1,2,2,2-tetrafluoroethoxy)methyl]-1,2,2,2-tetrafluoroethoxy]-1,1,2,2-tetrafluoro- (Nafion by-product 2)</p> <p>C₇H₂F₁₄O₅S</p> <p>463.9</p> <p>749836-20-2</p>

CAS—Chemical Abstracts Service, HFPO—DA—hexafluoropropylene oxide—dimer acid, NA—not applicable

^aIn Sun et al. (2016), this compound was presented as the linear perfluoro-3-methoxypropanoic acid isomer. However, it is more likely that environmental samples contain the branched isomer shown here and in Strynar et al. (2015).

^bIn Sun et al. (2016), this compound was presented as the linear perfluoro-4-methoxybutanoic acid (PFMOBA) isomer. However, it is more likely that environmental samples contain the branched isomer shown here.

analytical standards were available for GenX, but not for the other compounds shown in Table 2. As a result, aqueous concentrations of PFEAs other than GenX could be estimated only with the approach described in “Analytical Methods” later in this article. Efforts are

underway to custom-synthesize some of the compounds in Table 2, and The Chemours Company recently provided analytical standards for the compounds shown in Table 2 to the USEPA and some commercial laboratories.

TOXICITY OF GENX AND NORTH CAROLINA HEALTH GOAL

The bulk of toxicological research concerning PFASs has focused on PFOA and PFOS. While their production and use have been stopped by major manufacturers in the United States as a result of a stewardship program with the USEPA (2006), environmental concentrations of the legacy PFASs remain of concern. PFOA and PFOS can result from the breakdown of precursor PFASs (Houtz et al. 2013) and are environmentally persistent; therefore, continued study of their toxicity is warranted as they will continue to persist in the environment for decades to come. Accumulated evidence from studies of experimental animal models and of humans from highly exposed populations supports the conclusion that PFOA and PFOS, along with other carboxylate and sulfonate PFASs, are multi-system toxicants. In other words, exposure to PFASs is associated with toxicological findings in many types of tissues and systems. In fact, the evidence is sufficiently strong for PFOA that it has been classified as possibly carcinogenic to humans (Group 2B) by the International Agency for Research on Cancer (IARC 2016), and the US National Toxicology Program (NTP 2016) has classified both PFOA and PFOS as “presumed to be immune hazards to humans.” The USEPA HAL for PFOA and PFOS is based on developmental toxicity endpoints, indicating that exposure during the sensitive period of early life, including fetal life and the lactation period, may produce adverse health outcomes on growth and development (USEPA 2016a, 2016b). In addition, PFOA and PFOS are regarded as environmentally persistent, bioaccumulative, and toxic compounds (Wang et al. 2017). Compounds being used and designed to replace PFOA, PFOS, and other long-chain compounds therefore should ideally be less persistent, bioaccumulative, and toxic than the legacy compounds and be subjected to more stringent controls to prevent them from escaping or being released into the environment.

The regulatory environment for compounds being designed to replace PFOA, PFOS, and other long-chain compounds covered under the USEPA stewardship agreement is somewhat varied. For some compounds, testing performed under requirements of the Toxic Substances Control Act includes environmental degradation testing before commercialization and possible additional testing to demonstrate that the final degradation products are less bioaccumulative and less toxic than PFOA and other longer-chain PFASs (USEPA 2017a). However, publicly available and peer-reviewed published studies for many of the replacement compounds are far fewer than studies of PFOA and PFOS, so it is difficult to conclude that they lack the risk of adverse health effects. Without a deep knowledge of published studies on replacement compounds,

regulatory agencies—particularly those at the state level dealing with “hot spots” of contamination from industrial or other discharges of replacement PFASs, and a public demanding action to protect their health—often have to rely on the best available data from incomplete data sets when issuing advice to the public.

This was the case in North Carolina when the Cape Fear River was found to be contaminated with GenX and other PFASs with a paucity of published studies on their toxicity. The discovery of GenX in a drinking water source required that the North Carolina Department of Health and Human Services (DHHS) take action to protect the health of citizens exposed to GenX via their drinking water. The DHHS issued a health goal for GenX in July 2017 (DHHS 2017) of 140 ng/L. The health goal is a “non-regulatory, non-enforceable level of contamination below which no adverse health effects would be expected over a lifetime of exposure.” This designation is consistent with the PFOA/PFOS HAL derived by the USEPA. The study used by the DHHS to derive a health goal for GenX was one submitted in the European Union (EU) under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) program. The REACH program is a regulation of the EU adopted to improve protection of human health and the environment from the risks posed by chemicals (ECHA 2017). The GenX study was described in a report issued by the Netherlands National Institute for Public Health and the Environment (Beekman et al. 2016), which has a function analogous to the USEPA. Other studies in the published literature on the toxicity of GenX are limited in number but indicate that GenX likely produces toxicological outcomes similar to those of PFOA, albeit at different administered concentrations. Such outcomes include increased liver weight and the rodent “tumor triad,” i.e., the presence of tumors in the liver, pancreas, and testes (Rae et al. 2015). An immunotoxicity study of GenX in mice reported that GenX was less potent than PFOA at suppressing antibody production; 10 mg/kg/day was the “no observed adverse effect level” (NOAEL) and 100 mg/kg/day was the “lowest observed adverse effect level” (LOAEL) for GenX after 28 days of oral exposure (Rushing et al. 2017). For comparison, after 15 days of oral exposure to PFOA, values of 1.88 and 3.75 mg/kg/day were the NOAEL and LOAEL, respectively, for the same endpoint (DeWitt et al. 2008). NOAEL represents the highest administered dose that does not differ from the response of unexposed animals, whereas LOAEL represents the lowest administered dose that does differ from the response of unexposed animals. Both parameters often serve as points of departure for calculating HALs and other values protective of public health. A study by Rae et al. (2015) implied a LOAEL of 1 mg/kg/day for effects of GenX in livers and kidneys of male rats, indicating that effects may occur at lower

administered doses than those reported in the Rushing et al. (2017) study. Another study in male mice given a single dose of 1 mg/kg/day of GenX for four weeks demonstrated injury and alteration of genes associated with lipid metabolism in livers (Wang et al. 2016). However, this study focused only on a single administered dose, so the dose-responsiveness of these effects cannot be determined or applied to health goals.

To develop its provisional health goal for GenX, the North Carolina DHHS used a NOAEL of 0.1 mg/kg/day for liver single-cell necrosis (i.e., cell death in the liver) in male mice orally exposed to GenX for 28 days (summarized in Beekman et al. 2016). To account for various uncertainties associated with this NOAEL, the North Carolina DHHS adjusted this NOAEL by a factor of 10 for a “mouse to man” extrapolation, a factor of 10 for variability in the human population, and a factor of 10 for the use of a relatively short-term study (i.e., 28 days of exposure), thus deriving a reference dose (RfD) of 0.0001 mg/kg/day (0.1 mg/kg/day/1,000) (DHHS 2017). The RfD is similar to a health goal in that it is a dose of a chemical below which adverse health effects would not be expected over a lifetime of exposure to humans. To convert this RfD to a drinking water equivalent level (DWEL) that would be protective of bottle-fed infants, a subpopulation identified as particularly sensitive to effects of PFAS (recall that the USEPA HAL for PFOA and PFOS was based on the protection of developing fetuses as well as breastfed infants), the DHHS made the following assumptions (DHHS 2017):

- 7.8 kg of body weight for a bottle-fed infant
- 1.1 L/day of water intake for a bottle-fed infant
- 0.2 for the relative source contribution (proportion of the total daily exposure to a chemical that is attributed to or allocated to tap water [accounting for multiroute exposures] in calculating acceptable levels of chemicals in water [*Federal Register* 2014]).

On the basis of these assumptions, the DWEL was calculated as follows:

$$\begin{aligned} \text{DWEL} &= [(\text{RfD} \times \text{Body Weight}) / (\text{Intake})] \\ &\times \text{RSC} \times \text{mg to ng unit conversion} \\ &= [(0.0001 \text{ mg/kg/day} \times 7.8 \text{ kg}) / (1.1 \text{ L/day})] \\ &\times 0.2 \times 10^6 \text{ ng/mg} = 140 \text{ ng/L} \end{aligned} \quad (1)$$

The DWEL of 140 ng/L represents the current provisional health goal for GenX in North Carolina.

ANALYTICAL METHODS

Nontargeted analysis of Cape Fear River water by liquid chromatography/time-of-flight mass spectrometry (LC/TOF MS) led to the initial identification of PFEAs (Strynar et al. 2015). Details of the nontargeted analytical method are described in Strynar et al. (2015). Once

identified, PFEAs were incorporated into a targeted analytical method that relies on LC–tandem mass spectrometry (LC–MS/MS). The targeted analytical method follows a workflow similar to that in USEPA Method 537, which is designed to determine 14 legacy PFASs in drinking water. Several modifications to USEPA Method 537 are recommended to improve the recovery of GenX and other PFEAs and to ensure method accuracy in aqueous matrixes other than drinking water (McCord et al. 2018; USEPA 2017b, 2009b). Briefly, samples were collected in 1 L high-density polyethylene (HDPE) containers, preserved with 5 mL 1:1 nitric acid and stored at ambient temperature. Before analysis, sample volume was measured by pouring the entire contents of the sample bottle into a 1 L HDPE graduated cylinder. Ten milliliters of methanol was used to rinse the original sample bottle. The entire water sample was returned to the sample bottle containing methanol, and mass-labeled internal standards (ISs) for legacy PFASs and GenX were added to reach a target concentration of 200 ng/L. Bottles were then capped and their contents mixed. The entire sample (containing methanol and IS) was filtered through a GF/A filter¹ (1.7 µm pore size) into an HDPE vacuum flask and the filtrate returned to the original sample bottle. For solid-phase extraction (SPE), a 500 mL aliquot was removed from the sample bottle and processed through a weak anion-exchange (WAX), reverse-phase, water-wettable polymer cartridge² (Gebbinck et al. 2017; Heydebreck et al. 2015; Strynar et al. 2015). WAX cartridges improve the recovery of GenX and other PFEAs compared with the styrene-divinylbenzene SPE cartridges³ recommended in USEPA Method 537. Following extraction, PFASs were eluted from the SPE cartridge with 4 mL methanol:NH₄OH, and the eluate was subsequently evaporated to a volume of approximately 1 mL. After evaporation and before analysis, 100 µL of concentrated eluate was mixed with 300 µL of 2 mM ammonium acetate.

In this study, samples were analyzed using an ultra-performance liquid chromatograph⁴ (UPLC) interfaced with a triple quadrupole mass spectrometer.⁵ The UPLC was equipped with a PFAS analysis kit that includes a PFAS isolator column and stainless-steel tubing installed between the mixing chamber and the injection port. Using a 50 µL injection volume, PFASs were separated on a UPLC column⁶ (1.7 µm, 2.1 × 50 mm). Eluents were 95:5 percent volume per volume (v/v%) water: methanol with 2.5 mM ammonium acetate (A) and 5:95 v/v% water:methanol with 2.5 mM ammonium acetate (B). The eluent flow rate was 500 µL/min. A gradient starting with 90% A:10% B was used for the first 30 s, ramped to 15% A:85% B between 0.5 and 5 min, and to 100% B by 5.1 min, before ramping to 10% A:90% B between 7.0 and 7.1 min and staying at this eluent ratio until the analysis was complete at 9 min. Mass spectrometer settings for the PFEAs shown

TABLE 3 Mass spectrometer settings for PFEAs

Compound	[M - H] ⁻ (m/z)	Daughter (m/z)
GenX	329.0	284.9
M3GenX (Internal Standard)	332.0	286.9
PFMOAA	179.0	84.9
PFMOPrA	229.0	84.9
PFEOPrA/PFMOBA	279.0	84.9
PFO2HxA	245.0	84.9
PFO3OA	311.0	84.9
PFO4DA	377.0	84.9
Nafion byproduct 2	462.9	212.9

HFPO-DA—hexafluoropropylene oxide-dimer acid, PFEAs—perfluoroalkyl ether acids, PFEOPrA/PFMOBA—perfluoro-2-ethoxypropanoic acid/perfluoro-4-methoxybutanoic acid, PFMOAA—perfluoro-2-methoxyacetic acid, PFMOPrA—perfluoro-2-methoxypropanoic acid, PFO2HxA—perfluoro-3,5-dioxahexanoic acid, PFO3OA—perfluoro-3,5,7-trioxaoctanoic acid, PFO4DA—perfluoro-3,5,7,9-tetraxadecanoic acid

in Table 2 are summarized in Table 3. An exception was the Nafion byproduct 1, which has been detected only by high-resolution TOF MS to date (Strynar et al. 2015).

Because both native and mass-labeled forms of GenX are commercially available,⁷ GenX concentrations in water can be accurately determined using an isotope dilution approach. To develop a calibration curve, calibration standards were prepared in the concentration range 10–1,000 ng/L. After filtration, SPE, and LC–MS/MS analysis, area ratios (i.e., peak area for the native standard divided by the peak area for the IS) were plotted against known concentrations of the calibration standards. Standard curves were mathematically described by a concentration weighted (1/x) second-order polynomial fit. GenX concentrations in all samples, matrix spikes, and trip spikes were calculated from the area ratio and the standard curve. By using the isotope dilution approach, in which mass-labeled IS is added to the sample prior to filtration and SPE, inefficiencies in analyte recovery as well as ion suppression during LC–MS/MS analysis are corrected.

A major challenge for quantification of PFEAs other than GenX is the lack of commercially available authentic standards. For branched perfluoro-2-methoxypropanoic acid (PFMOPrA) and perfluoro-2-ethoxypropanoic acid (PFEOPrA) (Table 2), linear isomers (Table 2) are commercially available⁸ and were used to develop calibration curves; area ratios were calculated relative to the response for mass-labeled GenX. Concentrations of other PFEAs, for which no authentic standards were available, were estimated using Eq 2 by assuming that PFEA response factors in the mass spectrometer matched those of GenX. The resulting concentration estimates are therefore

uncertain—true concentrations may be higher or lower than the provided estimates, possibly by as much as a factor of 10 (McCord et al. 2018, USEPA 2017c).

$$\text{Conc. of Analyte} = \text{Conc. of GenX} \times \frac{\text{Peak Area of Analyte}}{\text{Peak Area of GenX}} \quad (2)$$

For quality assurance/quality control purposes, trip spikes, trip blanks, replicates, and matrix spikes need to be included with each sampling campaign. Details of the sampling, extraction, and analytical methods are described in USEPA Standard Operating Procedures (USEPA 2017b, 2009b).

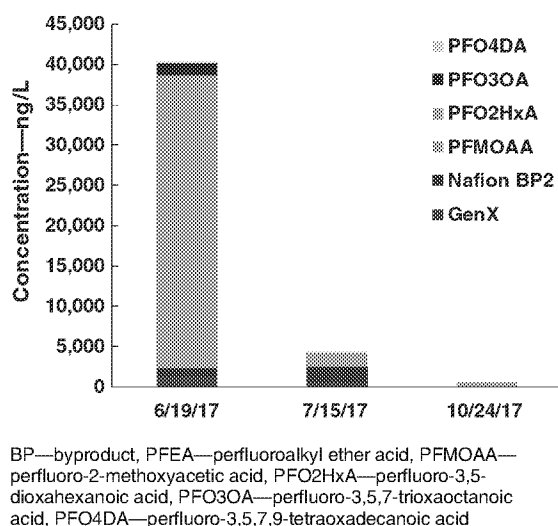
OCCURRENCE OF GENX AND RELATED COMPOUNDS

To date, only four peer-reviewed studies have documented the occurrence of GenX in surface water. Heydebreck et al. (2015) studied rivers in Germany, the Netherlands, and China and determined maximum GenX concentrations of 108, 91.5, and 3,830 ng/L, respectively. Elevated GenX concentrations were associated with sampling sites located downstream of industrial areas and known fluorochemical manufacturing plants. Strynar et al. (2015) first identified GenX along with other PFEAs (Table 2) in US surface waters, and Sun et al. (2016) reported GenX concentrations of up to 4,560 ng/L in the Cape Fear River of North Carolina. Most recently, Gebbink et al. (2017) conducted a detailed study of the Rhine River near a fluorochemical manufacturing facility in the Netherlands and determined a maximum GenX concentration of 812 ng/L at the first sampling location downstream of the manufacturing plant.

Only two studies have documented the concentration of GenX in drinking water. Sun et al. (2016) found a GenX concentration of 474 ng/L in finished drinking water derived from the Cape Fear River, while Gebbink et al. (2017) determined a maximum GenX concentration of 11 ng/L in Dutch drinking water that was sourced from a GenX-impacted river. Sun et al. (2016) further documented that GenX constituted only a small fraction of the total concentration of targeted PFEAs in both raw and finished drinking water. In the absence of analytical standards for PFEAs other than GenX, the authors compared chromatographic peak areas and determined that the dominant PFEA was perfluoro-2-methoxyacetic acid (PFMOAA; peak area ~100 times that of GenX) followed by perfluoro-3,5-dioxahexanoic acid (PFO2HxA; peak area ~25 times that of GenX) and perfluoro-3,5,7-trioxaoctanoic acid (PFO3OA; peak area ~5 times that of GenX).

After the June 8, 2017, publication of a newspaper article (Hagerty 2017) and a June 15, 2017, meeting between local officials in the lower Cape Fear River basin and representatives from the fluorochemical

FIGURE 3 Evolution of PFEA concentrations in Cape Fear River water at a drinking water intake located approximately 90 mi downstream from a fluorochemical manufacturer



manufacturer, the manufacturer agreed to stop discharging process wastewater containing GenX in late June 2017. As shown in Figure 3, the sum concentration of targeted PFEAs in the Cape Fear River at a drinking water intake located approximately 90 mi downstream from the manufacturer was estimated to be about 40,000 ng/L before capture of the GenX-containing process wastewater, with contributions from PFMOAA >> PFO2HxA > PFO3OA ~GenX > Nafion byproduct 2 > PFO4DA. When the manufacturer began to capture process wastewater containing GenX, the sum concentration of targeted PFEAs in the river dropped sharply to an estimated concentration of approximately 4,200 ng/L by July 15, 2017 (Figure 3). While the overall PFEA levels decreased, the estimated concentration of Nafion byproduct 2 increased from June 19 to July 15, 2017 (Figure 3). As a result, the North Carolina Department of Environmental Quality and USEPA characterized additional process waste streams with a focus on Nafion byproducts. In late October 2017, the fluorochemical manufacturer agreed to capture process wastewater containing Nafion byproducts, which yielded an additional drop in the sum concentration of targeted PFEAs in both raw water (Figure 3) and finished drinking water (Figure 4). From late October through early December 2017, the total concentration of targeted PFEAs in the finished drinking water remained in the 200–400 ng/L range. Also shown in Figure 4 is a spike in GenX concentrations to 257 ng/L on Oct. 20, 2017, which resulted from a spill at the manufacturing facility.

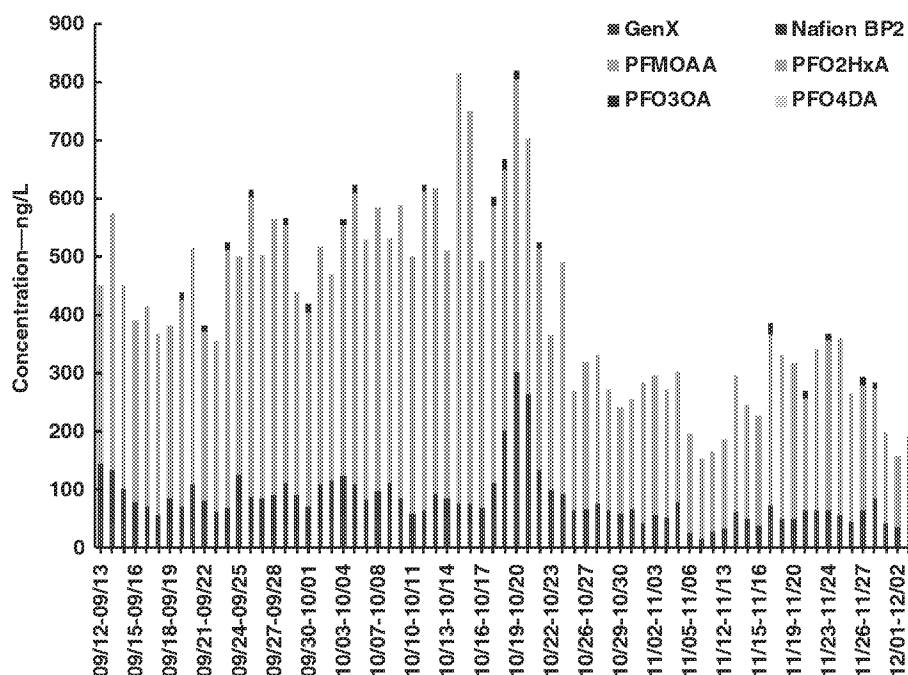
To determine whether changes in PFEA concentrations were primarily a result of source reduction or changes in streamflow, streamflow data were obtained for the sampling dates shown in Figure 3. On Oct. 24, 2017, streamflow at the Cape Fear River sampling location was approximately 900 ft³/s, which was lower than those on June 19, 2017 (~2,300 ft³/s) and on July 15, 2017 (~1,400 ft³/s). Thus, PFEA mass flows dropped more substantially than PFEA concentrations shown in Figure 3. While PFEA levels in the river have dropped dramatically since June 2017, questions remain about the sources of the remaining PFEAs. Possible options include discharge of contaminated groundwater (NC DEQ 2017b) from below the manufacturing facility into the Cape Fear River, stormwater runoff from the manufacturing site and its surroundings, and desorption from river sediment. It should be noted that no PFEAs were detected in the Cape Fear River at the intake of a drinking water treatment plant located approximately 20 mi upstream of the fluorochemical manufacturer.

EFFECTIVENESS OF DRINKING WATER TREATMENT PROCESSES FOR THE REMOVAL OF GENX AND RELATED COMPOUNDS

To date, limited information is available on the effectiveness of water treatment processes for the removal of GenX and other PFEAs. As illustrated in Figure 5, GenX was not measurably removed by conventional surface water treatment processes (coagulation, flocculation, sedimentation, filtration, disinfection with free chlorine) and by several advanced water treatment processes, including raw and settled water ozonation, biofiltration, and disinfection with medium-pressure ultraviolet (UV) lamps at a water treatment plant (WTP) located approximately 90 mi downstream of the fluorochemical plant. Sun et al. (2016) found similar results for GenX and other PFEAs at the same WTP. In Figure 5, the time lag between raw and finished water concentration data was approximately one day, which reflects the hydraulic residence time of the WTP. The data in Figure 5 further illustrate that source reduction efforts by the manufacturer, which began in the third week of June and continued into July, were effective in lowering GenX concentrations in raw and finished water to below North Carolina's health goal for GenX of 140 ng/L by the end July 2017.

Activated carbon adsorption. Both powdered and granular activated carbon (PAC and GAC, respectively) are commonly used in drinking water treatment. To evaluate PFEA removal by PAC, Sun et al. (2016) selected a thermally activated wood-based PAC that was previously shown to be effective for PFAS removal (Dudley et al. 2015). For GenX, 30% removal was achieved with a PAC dose of 60 mg/L. For reference, the same PAC dose led to 80% PFOA and >95% PFOS removal.

FIGURE 4 Time series of PFEA concentrations in finished drinking water following conventional surface water treatment



BP—byproduct, PFEA—perfluoroalkyl ether acid, PFMOAA—perfluoro-2-methoxyacetic acid, PFO2HxA—perfluoro-3,5-dioxahexanoic acid, PFO3OA—perfluoro-3,5,7-trioxaocanoic acid, PFO4DA—perfluoro-3,5,7,9-tetraoxadecanoic acid

Each bar represents results for a 24 h composite sample.

Short-chain PFEAs, such as PFMOPrA and PFO2HxA, were essentially nonadsorbable, even when 100 mg/L PAC was added to raw Cape Fear River water (Sun et al. 2016).

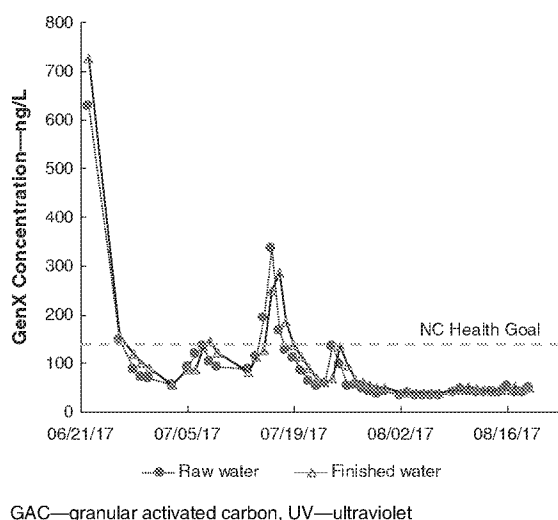
Because dissolved organic matter (DOM) has a strong negative effect on PFAS adsorption, employing GAC after DOM removal by coagulation is expected to be more effective for PFEA removal than the addition of PAC to raw water. Total organic carbon (TOC) concentrations in the Cape Fear River range from about 6 to 9 mg/L, while TOC concentrations in coagulated/settled Cape Fear River water are typically about 2 mg/L. For this study, PFEA removal was studied in a post-filter GAC adsorber that contained regenerated subbituminous coal-based GAC. The empty bed contact time (EBCT) averaged 14 min during the course of the study, and the plant treated water for approximately 9 h/day. Freshly regenerated GAC had been put into service on Mar. 22, 2017, and GAC influent and effluent samples were collected from June 19 to July 24, 2017.

As shown in Figure 6, GenX had reached 7% breakthrough after approximately 3,500 bed volumes (BV) of water had been treated, and it reached 74% breakthrough after approximately 5,000 BV had been treated. The breakthrough curve for PFO2HxA was similar

to that of GenX, while higher removal percentages were obtained for PFO3OA and PFO4DA. Nafion byproduct 2, a seven-carbon diether (Table 2), was effectively removed during the study period. The full-scale results shown in Figure 6 are consistent with pilot-scale data collected at a neighboring utility that obtains Cape Fear River water from the same intake location. In the pilot study, which evaluated three types of GAC at an EBCT of 10 min and at two locations in the plant (following settled-water ozone and following biofiltration), GenX was removed to below the method reporting limit (MRL) of 5 ng/L for the first 2,000 BV, but substantial GenX breakthrough (35–64%) was observed after approximately 5,000 BV had been treated (CFPUA 2017).

Both the full-scale and pilot-scale results illustrate that GAC is only somewhat effective for controlling GenX in the context of treating coagulated Cape Fear River water. Recognizing that the adsorbability of PFASs decreases with decreasing perfluorinated carbon chain length (Xiao et al. 2017, Sun et al. 2016, Dudley et al. 2015), GAC will be only marginally effective for shorter-chain PFEAs such as PFMOAA, PFMOPrA, and PFEOPrA as well as the diether PFO2HxA. For Nafion byproduct 2, effective GAC performance can be expected

FIGURE 5 Concentrations of GenX in raw and finished water of a treatment plant employing raw water ozonation, coagulation/flocculation/ sedimentation, settled water ozonation, GAC biofiltration, medium-pressure UV disinfection, and free chlorine disinfection

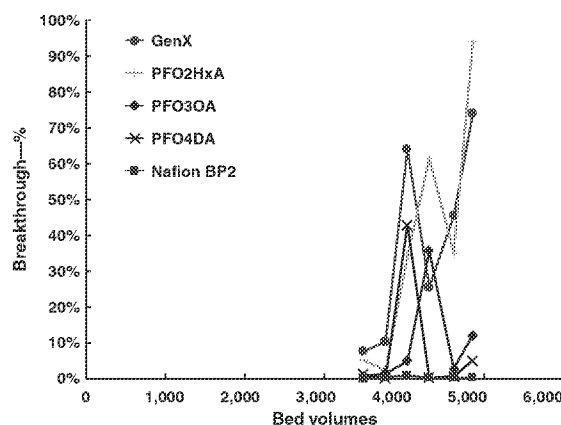


Data from North Carolina Department of Environmental Quality (2017a) and CFPUA (2017)

for at least 5,000 BV, but data collected at the top sampling port of the full-scale adsorber as well as data from the pilot study show substantial breakthrough of the Nafion byproduct 2 in the range 10,000–15,000 BV (>82% breakthrough at full scale, >74% breakthrough at pilot scale). For reference, pilot-scale data showed PFOA breakthrough of >20% after about 9,000 BV and PFOS breakthrough of >20% after 13,500 BV (CFPUA 2017). The latter results illustrate that GAC treatment of coagulated surface water with a TOC concentration of about 2 mg/L can be costly even for the control of PFOA and PFOS.

An additional concern with GAC adsorption processes is the potential for desorption when PFEA concentrations change in the source water and/or more strongly adsorbing compounds displace weakly adsorbed PFEAs as the mass transfer zones of the more strongly adsorbing compounds migrate through the GAC bed. In this study, the first scenario applied; PFEA concentrations in the source water decreased dramatically as a result of source reduction efforts. At the beginning of the evaluation period (June 19, 2017; ~3,500 BV of water treated), PFMOAA removal was approximately 70%. As PFMOAA concentrations in the GAC

FIGURE 6 PFEA breakthrough curves for a full-scale post-filter GAC contactor



BP—byproduct, EBCT—empty bed contact time, GAC—granular activated carbon, PFEA—perfluoroalkyl ether acid, PFO2HxA—perfluoro-3,5-dioxahexanoic acid, PFO3OA—perfluoro-3,5,7-trioxaoctanoic acid, PFO4DA—perfluoro-3,5,7,9-tetraoxadecanoic acid

GAC: regenerated sub-bituminous coal-based, EBCT: 14 min

influent decreased from approximately 26,000 to approximately 680 ng/L, PFMOAA removal quickly ceased, and during the last three weeks of the monitoring period, PFMOAA levels in the GAC effluent were approximately 10 times those measured in the GAC influent.

Apart from the monitored adsorber, the utility operates two additional GAC adsorbers, and the finished water is the blended effluent from all three GAC adsorbers. At the beginning of the sampling campaign, the three post-filter GAC adsorbers, which were operated in parallel (EBCT ~14 min each), had treated approximately 3,500, 11,000, and 15,000 BV of water, respectively. Daily composite samples of raw and finished water were collected from June 22 to July 26, 2017. On average, GenX concentrations in the plant effluent were 28% higher than those in the plant influent. Given that the adsorber containing the youngest GAC was able to remove GenX during the study period (Figure 6), the results suggest that the two adsorbers containing older GAC were desorbing GenX.

Finally, questions about the management of spent GAC with adsorbed PFASs remain. Management options for spent GAC include landfilling, incineration, and thermal reactivation (e.g., Pancras et al. 2016, Duan et al. 2014, Chowdhury et al. 2013). In the case of landfilling, the PFAS desorption potential from spent GAC needs to be studied. Landfill leachate is one vector

TABLE 4 Effectiveness of drinking water treatment processes for PFAS removal

Treatment	PFEAs (e.g., GenX)	Short-Chain PFASs (e.g., PFBA)	Long-Chain PFASs (e.g., PFOA, PFOS)	Challenges
Coagulation/ sedimentation/ filtration	Not effective	Not effective	Not effective at conditions relevant to drinking water treatment	NA
Chlorination/ chloramination	Not effective	Not effective	Not effective	NA
Ozonation	Not effective	Not effective	Not effective	NA
UV/H ₂ O ₂	Not evaluated, but not expected to be effective	Not effective	Not effective	NA
PAC adsorption	Moderately effective (e.g., PFO4DA) to not effective (e.g., PFMOAA)	Not effective	Moderately effective to somewhat effective	Performance strongly dependent on activated carbon properties and background water matrix; spent PAC needs to be managed
GAC adsorption	Moderately effective (e.g., Nafion byproduct 2) to somewhat effective (e.g., GenX, PFO2HxA); additional data needed, bench- and pilot-testing is ongoing	Moderately effective (groundwater) to somewhat effective (surface water)	Very effective (groundwater) to moderately effective (surface water)	See PAC; desorption can diminish effectiveness when influent concentrations are variable; spent GAC needs to be managed; fate of PFASs during thermal regeneration not well understood
Anion exchange	Under evaluation, very effective for Nafion byproduct 2, moderately effective for GenX; removal of short-chain PFEAs such as PFMOAA needs further study	Moderately effective to somewhat effective	Very effective to moderately effective	Performance strongly dependent on resin properties; background water matrix effects largely unexplored; spent resin or spent regenerant needs to be managed
High-pressure membranes (nanofiltration, reverse osmosis)	Not evaluated, but likely effective based on results obtained with short-chain PFASs and household reverse osmosis systems	Effective	Effective	High energy requirement; membrane fouling; concentrate needs to be managed

GAC—granular activated carbon, H₂O₂—hydrogen peroxide, NA—not applicable, PAC—powdered activated carbon, PFASs—per- and polyfluoroalkyl substances, PFBA—perfluorobutanoic acid, PFEAs—perfluoroalkyl ether acids, PFMOAA—perfluoro-2-methoxyacetic acid, PFO2HxA—perfluoro-3,5-dioxahexanoic acid, PFO4DA—perfluoro-3,5,7,9-tetraoxadecanoic acid, PFOA—perfluorooctanoic acid, PFOS—perfluorooctane sulfonic acid, UV—ultraviolet

through which PFASs are reintroduced into the environment (e.g., Lang et al. 2017) if landfill leachate is shipped to wastewater treatment plants or is aerosolized. Incineration of spent GAC would have to be conducted at temperatures that are sufficiently high to mineralize PFASs. During thermal reactivation, PFASs may not be completely mineralized at temperatures used to reactivate GAC (Watanabe et al. 2018, 2016). While the thermal reactivation process oxidizes adsorbed background organic matter and thus effectively restores the adsorption capacity of GAC, the fate of PFASs during thermal reactivation and subsequent use of reactivated GAC require further study (Stroo et al. 2017).

Anion exchange. The effectiveness of anion-exchange resins for PFEA removal has not been reported in the peer-reviewed literature. However, several studies have evaluated the removal of long- and short-chain PFASs by anion-exchange resins (McCleaf et al. 2017,

Woodard et al. 2017, Zaggia et al. 2016, Dudley et al. 2015). For example, Woodard et al. (2017) showed that the number of bed volumes to the onset of PFAS breakthrough was larger for anion exchange than for GAC treatment. Differences were more pronounced for longer-chain PFASs compared with shorter-chain PFASs, and more pronounced for sulfonic acids compared with carboxylic acids with the same number of perfluorinated carbons. To evaluate PFEA removal, a pilot study evaluating anion-exchange resins at a utility in the lower Cape Fear River basin is ongoing. Pilot columns (EBCT = 1.5 min) showed that GenX was removed to below the method reporting limit of 5 ng/L for at least 27,400 BV, and GenX removals for the two tested resins were 38 and 75% after treating 62,500 BV (CFPUA 2017). Also, no detectable breakthrough was observed for Nafion byproduct 2, PFOA, or PFOS after 62,500 BV of water had been treated. While these

results are encouraging, further evaluation is needed before life cycle costs of anion exchange and GAC treatment options can be compared. Similar to GAC, management of spent anion-exchange resin requires careful consideration. Spent resin can be regenerated on site, landfilled, or incinerated. On-site resin regeneration would require the development of a suitable regeneration strategy that may require both brine and an organic solvent (McCleaf et al. 2017, Woodard et al. 2017, Zaggia et al. 2016, Dudley et al. 2015) and management of the spent brine that contains high levels of PFASs. Considerations for landfilling and incineration would be the same as those for GAC.

High-pressure membranes. On the basis of high removal percentages obtained for short-chain PFASs, such as perfluorobutanoic acid (PFBA) (Appleman et al. 2013, Lipp et al. 2010), it is expected that nanofiltration and reverse osmosis processes effectively remove the PFEAs shown in Table 2. Factors that positively influence removal by high-pressure membranes are increasing pollutant size and charge. Formula weights of the PFEAs in Table 2 range from 180 to 464 Da, and the formula weight of PFBA is 214 Da. All PFEAs in Table 2 are predicted to be strong acids and are expected to be present as anions at typical water treatment pH values. Data from under-the-sink reverse osmosis systems from homes of residents in the communities affected by the PFEA contamination confirmed that GenX was removed to below method reporting limits, and other PFEAs, including PFMOAA, were effectively removed as well (Merrill 2018). Apart from high energy demand and membrane fouling, a key challenge with high-pressure membranes in a municipal-scale treatment context is management of the retentate, which contains high levels of PFASs and salts.

OVERVIEW OF TREATMENT TECHNOLOGIES FOR PFAS REMOVAL

An overview of drinking water treatment technologies and their effectiveness for PFAS removal is provided in Table 4. The information in Table 4 is based on bench- and pilot-scale tests, as well as information from full-scale drinking water treatment plants (Woodard et al. 2017, Sun et al. 2016, Zaggia et al. 2016, Dudley et al. 2015, Appleman et al. 2014, Rahman et al. 2014, Vecitis et al. 2009).

IMPLICATIONS

USEPA's UCMR 3 data illustrate that 4% of 4,920 public water systems distributed water that contained at least one of the six targeted PFAS compounds at detectable levels. Furthermore, the UCMR 3 data suggest that at least six million US residents consume drinking water that contains combined PFOS and PFOA at levels above the 70 ng/L HAL (Hu et al. 2016). While the UCMR 3 data collection effort provided the first nationwide

documentation of PFAS occurrence in public water systems, it underestimated the overall PFAS exposure through drinking water in a number of important ways, including (1) method reporting limits for the UCMR 3 were high, (2) public water systems serving <10,000 people were not evaluated in a comprehensive manner, (3) nonpublic water systems and private wells were not considered, and (4) only six PFASs were targeted in UCMR 3, such that information about short-chain perfluoroalkyl carboxylic acids and emerging PFASs, such as GenX and the other PFEAs discussed here, is lacking. With the phasing out of the production and use of long-chain PFASs such as PFOA and PFOS in the United States, fluorochemical manufacturers have shifted their production to shorter-chain PFASs (e.g., perfluoroalkyl carboxylic acids with chain length ≤ 6) and fluorinated replacements (e.g., GenX, ADONA,⁹ F53-B¹⁰). A challenge for drinking water providers and state regulators is that information about many fluorinated replacements is considered confidential business information. Often the chemical structures, basic physicochemical properties, toxicological data, production volumes, and locations of use are unknown. As a result, it is difficult to protect drinking water sources through NPDES discharge permits and air quality permits. In addition, the production of fluorochemicals results in a large number of per- and polyfluorinated byproducts that are largely unknown. To ensure that PFAS contamination is absent, public water systems, including the ones with UCMR 3 results below 70 ng/L for PFOA and PFOS or nondetect/low for the six targeted PFASs, should therefore consider screening their source and finished water for a wider range of PFASs.

ACKNOWLEDGMENT

The authors would like to thank Mark Strynar, Andrew Lindstrom, and James McCord at the USEPA, Research Triangle Park, N.C., for sharing their expertise and for opening their laboratory to Zachary R. Hopkins and Mei Sun. The authors would also like to thank utility staff in the lower Cape Fear basin for collecting and delivering samples to NC State University. Partial support for Hopkins and Sun was provided through the National Science Foundation (Award no. 1550222).

ENDNOTES

¹GF/A glassfiber filters, Whatman, GE Healthcare, Chicago, Ill.

²WAX SPE cartridges, Waters, Milford, Mass.

³HLB SPE cartridges, Waters, Milford, Mass.

⁴ACQUITY UPLC System, Waters, Milford, Mass.

⁵Quattro Premier XE, Waters, Milford, Mass.

⁶ACQUITY UPLC BEH C18 column, Waters, Milford, Mass.

⁷Wellington Laboratories, Guelph, Ont.

⁸Synquest Laboratories, Alachua, Fla.

⁹ADONA: 4,8-dioxa-3H-perfluorononanoic acid

¹⁰F53-B: 2-[[6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyl]oxyl]-1,1,2,2-tetrafluoroethanesulfonic acid, potassium salt

ABOUT THE AUTHORS



Zachary R. Hopkins is a PhD candidate in the Department of Civil, Construction, and Environmental Engineering, North Carolina State University, Raleigh. He received a BS degree in chemical engineering in 2012 and an MS degree in civil and

environmental engineering in 2014 from the University of Maryland, Baltimore County. He has studied ozonation and advanced oxidation processes for the treatment of emerging contaminants, such as ultraviolet filters, antibiotics, and 1,4-dioxane. Beginning in 2017, his research began to focus on the occurrence and treatment of legacy and emerging per- and polyfluoroalkyl substances (PFASs). He presented results of his 1,4-dioxane research at the 2017 AWWA Annual Conference and Exposition. More recently, he was awarded first place in the student poster competition at the NC AWWA-WEA 97th Annual Conference, where he presented results of his PFAS research. Hopkins is a member of AWWA and the American Chemical Society. **Mei Sun** is an assistant professor at the University of North Carolina at Charlotte. **Jamie C. DeWitt** is an associate professor at East Carolina University, Greenville, N.C. **Detlef R.U. Knappe** (to whom correspondence may be addressed) is a professor in the Department of Civil, Construction, and Environmental Engineering at North Carolina State University; knappe@ncsu.edu.

<https://doi.org/10.1002/awwa.1073>

PEER REVIEW

Date of submission: 12/20/17

Date of acceptance: 04/02/18

REFERENCES

- Appleman, T.D.; Higgins, C.P.; Quiñones, O.; Vanderford, B.J.; Kolstad, C.; Zeigler-Holady, J.C.; & Dickenson, E.R.V., 2014. Treatment of Poly- and Perfluoroalkyl Substances in U.S. Full-Scale Water Treatment Systems. *Water Research*, 51: Supplement C:246. <https://doi.org/10.1016/j.watres.2013.10.067>.
- Appleman, T.D.; Dickenson, E.R.V.; Bellona, C.; & Higgins, C.P., 2013. Nanofiltration and Granular Activated Carbon Treatment of Perfluoroalkyl Acids. *Journal of Hazardous Materials*, 260: Supplement C:740. <https://doi.org/10.1016/j.jhazmat.2013.06.033>.
- Beekman, M.; Zweepers, P.; Muller, A.; de Vries, W.; Janssen, P.; & Zeilmaker, M., 2016. *Evaluation of Substances Used in the GenX Technology by Chemours, Dordrecht*, RIVM Letter Report 2016-0174. National Institute for Public Health and the Environment, Bilthoven, the Netherlands.
- Bilott, R., 2017. *Letter to West Virginia Department of Environmental Protection: Request for Information/Action Relating to GenX Materials Used and Released From DuPont's/Chemours' Washington Works Facility in Wood County, West Virginia*. NPDES Permit WV0001279/Consent Order No. 7418. www.documentcloud.org/documents/3921034-Request-for-Information-Relating-to-GenX-Materials.html (accessed Dec. 18, 2017).
- CFPUA (Cape Fear Public Utility Authority), 2017. GenX Information. CFPUA, Wilmington, N.C. www.cfpua.org/CivicAlerts.aspx?CID=18 (accessed Dec. 16, 2017).
- Chowdhury, Z.K.; Summers, R.S.; Westerhoff, G.P.; Leto, B.J.; Nowack, K.O.; & Corwin, C.J., 2013. *Activated Carbon—Solutions for Improving Water Quality*. Water Research Foundation, Denver.
- Davis, K.L.; Aucoin, M.D.; Larsen, B.S.; Kaiser, M.A.; & Hartten, A.S., 2007. Transport of Ammonium Perfluorooctanoate in Environmental Media Near a Fluoropolymer Manufacturing Facility. *Chemosphere*, 67:10:2011. <https://doi.org/10.1016/j.chemosphere.2006.11.049>.
- DeWitt, J.C.; Copeland, C.B.; Strynar, M.J.; & Luebke, R.W., 2008. Perfluorooctanoic Acid-Induced Immunomodulation in Adult C57BL/6J or C57BL/6N Female Mice. *Environmental Health Perspectives*, 116:5:644. <https://doi.org/10.1289/ehp.10896>.
- DHHS (Department of Health and Human Services), 2017. Questions and Answers Regarding North Carolina Department of Health and Human Services Updated Risk Assessment for GenX (Perfluoro-2-Propoxypropanoic Acid). NC DHHS, Raleigh, N.C. <https://files.nc.gov/ncdeq/GenX/NC%20DHHS%20Risk%20Assessment%20FAQ%20Final%20Clean%20071417%20PM.pdf> (accessed Dec. 18, 2017).
- Duan, F.; Chyang, C.S.; Wang, J.T.; & Tso, J., 2014. Spent Activated Carbon Combustion in a Fluidized-Bed Combustor. *Energy & Fuels*, 28:2:1463. <https://doi.org/10.1021/ef401743j>.
- Dudley, L.A.; Arevalo, E.C.; & Knappe, D.R.U., 2015. *Removal of Perfluoroalkyl Substances by PAC Adsorption and Anion Exchange*. Water Research Foundation, Denver.
- ECHA (European Chemicals Agency), 2017. Understanding REACH. ECHA, Helsinki, Finland. <https://echa.europa.eu/regulations/reach/understanding-reach> (accessed Dec. 18, 2017).
- Federal Register*, 2014. Announcement of Preliminary Regulatory Determinants for Contaminants on the Third Drinking Water Contaminant Candidate List: Proposed Rule. www.gpo.gov/fdsys/pkg/FR-2014-10-20/html/2014-24582.htm (accessed Dec. 18, 2017).
- Gebbink, W.A.; van Asseldonk, L.; & van Leeuwen, S.P.J., 2017. Presence of Emerging Per- and Polyfluoroalkyl Substances (PFASs) in River and Drinking Water Near a Fluorochemical Production Plant in the Netherlands. *Environmental Science & Technology*, 51:19:11057. <https://doi.org/10.1021/acs.est.7b02488>.
- Hagerty, V., 2017. Toxin Taints CFPUA Drinking Water. *Wilmington Star News*, June 7, 2017. www.starnewsonline.com/news/20170607/toxin-taints-cfpua-drinking-water/1 (accessed Dec. 18, 2017).
- Heydebreck, F.; Tang, J.; Xie, Z.; & Ebinghaus, R., 2015. Alternative and Legacy Perfluoroalkyl Substances: Differences Between European and Chinese River/Estuary Systems. *Environmental Science & Technology*, 49:14:8386. <https://doi.org/10.1021/acs.est.5b01648>.
- Houtz, E.F.; Higgins, C.P.; Field, J.A.; & Sedlak, D.L., 2013. Persistence of Perfluoroalkyl Acid Precursors in AFFF-Impacted Groundwater and Soil. *Environmental Science & Technology*, 47:15:8187. <https://doi.org/10.1021/es4018877>.
- Hu, X.C.; Andrews, D.Q.; Lindstrom, A.B.; Bruton, T.A.; Schaidler, L.A.; Grandjean, P.; Lohmann, R.; et al., 2016. Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater

- Treatment Plants. *Environmental Science & Technology Letters*, 3: 10:344. <https://doi.org/10.1021/acs.estlett.6b00260>.
- IARC (International Agency for Research on Cancer), 2016. *Some Chemicals Used as Solvents and in Polymer Manufacture*. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, No. 110. World Health Organization, Lyon, France.
- Lang, J.R.; Allred, B.M.; Field, J.A.; Levis, J.W.; & Barlaz, M.A., 2017. National Estimate of Per- and Polyfluoroalkyl Substance (PFAS) Release to U.S. Municipal Landfill Leachate. *Environmental Science & Technology*, 51:4:2197. <https://doi.org/10.1021/acs.est.6b05005>.
- Lindstrom, A.B.; Galloway, J.; Strynar, M.J.; Knappe, D.; Sun, M.; & Weavers, L.K., 2017. *Emerging Per- and Polyfluoroalkyl Substances (PFAS)*. Highly Fluorinated Compounds—Social and Scientific Discovery, Northeastern University Social Science Environmental Health Research Institute, Boston.
- Lerner, S., 2016. A Chemical Shell Game: How Dupont Concealed the Dangers of the New Teflon Toxin. *The Intercept*, Mar. 3, 2016. <https://theintercept.com/2016/03/03/how-dupont-concealed-the-dangers-of-the-new-teflon-toxin/> (accessed Dec. 18, 2017).
- Lipp, P.; Sacher, F.; & Baldauf, G., 2010. Removal of Organic Micro-Pollutants During Drinking Water Treatment by Nanofiltration and Reverse Osmosis. *Desalination and Water Treatment*, 13:1–3:226. <https://doi.org/10.5004/dwt.2010.1063>.
- McCleaf, P.; Englund, S.; Östlund, A.; Lindegren, K.; Wiberg, K.; & Ahrens, L., 2017. Removal Efficiency of Multiple Poly- and Perfluoroalkyl Substances (PFASs) in Drinking Water Using Granular Activated Carbon (GAC) and Anion Exchange (AE) Column Tests. *Water Research*, 120:77. <https://doi.org/10.1016/j.watres.2017.04.057>.
- McCord, J.; Newton, S.; & Strynar, M., 2018. Validation of Quantitative Measurements and Semi-quantitative Estimates of Emerging Perfluoroethercarboxylic Acids (PFECAs) and Hexafluoropropylene Oxide Acids (HFPOAs). *Journal of Chromatography A*, 1551:52.
- Merrill, J., 2018. Removal of Per- and Polyfluoroalkyl Substances by Household Water Treatment Devices in the Cape Fear River Watershed of North Carolina. Undergraduate Thesis. North Carolina State University, Raleigh, N.C.
- NC DEQ (North Carolina Department of Environmental Quality), 2018a. GenX Update. Select Committee on North Carolina River Quality. www.ncleg.net/documentsites/committees/house2017-185/Meetings/6%20-%20Mar%2022%202018/River%20Water%20Quality%20DEQ.pdf (accessed Mar. 26, 2018).
- NC DEQ, 2018b. DEQ GenX Update. House Select Committee on River Quality. Apr. 26, 2018. www.ncleg.net/documentsites/committees/house2017-185/Meetings/7%20-%20April%2026%202018/DEQ%20Update%20on%20GenX.pdf (accessed May 19, 2018).
- NC DEQ, 2018c. Expanded PFAS Sample Analysis. https://files.nc.gov/ncdeq/GenX/DEQ.PWW_Expanded.PFAS_Summary_WEB-POST_030818.pdf (accessed Mar. 26, 2018).
- NC DEQ, 2017a. GenX Sampling Sites. <http://deq.nc.gov/news/hot-topics/genx-investigation/genx-sampling-sites> (accessed Dec. 18, 2017).
- NC DEQ, 2017b. Select Committee on North Carolina River Quality. www.ncleg.net/documentsites/committees/house2017-185/Meetings/3%20-%20Nov%2030%202017/DEQ%20Final%20PowerPoint%20Pres.pdf (accessed Dec. 18, 2017).
- NJ DEP (New Jersey Department of Environmental Protection), 2017. *Maximum Contaminant Level Recommendation for Perfluorooctanoic Acid in Drinking Water*. NJ DEP Drinking Water Quality Institute, Trenton, N.J.
- NJ DEP, 2015. *Maximum Contaminant Level Recommendations for Perfluorononanoic Acid in Drinking Water*. NJ DEP Drinking Water Quality Institute, Trenton, N.J.
- NTP (National Toxicology Program), 2016. *Monograph on Immunotoxicity Associated With Exposure to Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS)*. NTP, Research Triangle Park, N.C.
- Oppenheimer, J.; Hsung, R.P.; Li, H.; Lu, T.; & Wie, Y., 2007. Hexafluoropropene Oxide. *Encyclopedia of Reagents for Organic Synthesis 1*. John Wiley & Sons, New York. <https://doi.org/10.1002/047084289X.rn00768>.
- Pancras, T.; Schrauwen, G.; Held, T.; Baker, K.; Ross, I.; & Slenders, H., 2016. *Environmental Fate and Effects of Poly- and Perfluoroalkyl Substances (PFAS)*. Concawe, Brussels.
- Rae, J.M.C.; Craig, L.; Slone, T.W.; Frame, S.R.; Buxton, L.W.; & Kennedy, G.L., 2015. Evaluation of Chronic Toxicity and Carcinogenicity of Ammonium 2,3,3,3-Tetrafluoro-2-(Heptafluoropropoxy)-Propanoate in Sprague-Dawley Rats. *Toxicology Reports*, 2:939. <https://doi.org/10.1016/j.toxrep.2015.06.001>.
- Rahman, M.F.; Peldszus, S.; & Anderson, W.B., 2014. Behaviour and Fate of Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) in Drinking Water Treatment: A Review. *Water Research*, 50: Supplement C:318.
- Rushing, B.R.; Hu, Q.; Franklin, J.N.; McMahan, R.L.; Dagnino, S.; Higgins, C.P.; Strynar, M.J.; & DeWitt, J.C., 2017. Evaluation of the Immunomodulatory Effects of 2,3,3,3-Tetrafluoro-2-(Heptafluoropropoxy)-Propanoate in C57BL/6 Mice. *Toxicological Sciences*, 156:1:179. <https://doi.org/10.1093/toxsci/kfw251>.
- Stroo, H.; Leeson, A.; Deeb, R.; Higgins, C.; Mills, M.; Patton, C.; Porter, R. et al., 2017. *SERDP and ESTCP Workshop on Research and Demonstration Needs for Management of AFFF-Impacted Sites*. Department of Defence.
- Strynar, M.; Dagnino, S.; McMahan, R.; Liang, S.; Lindstrom, A.; Andersen, E.; McMillan, L.; Thurman, M.; Ferrer, I.; & Ball, C., 2015. Identification of Novel Perfluoroalkyl Ether Carboxylic Acids (PFECAs) and Sulfonic Acids (PFESAs) in Natural Waters Using Accurate Mass Time-of-Flight Mass Spectrometry (TOFMS). *Environmental Science & Technology*, 49:19:11622. <https://doi.org/10.1021/acs.est.5b01215>.
- Sun, M.; Arevalo, E.; Strynar, M.; Lindstrom, A.; Richardson, M.; Kearns, B.; Pickett, A.; Smith, C.; & Knappe, D.R.U., 2016. Legacy and Emerging Perfluoroalkyl Substances Are Important Drinking Water Contaminants in the Cape Fear River Watershed of North Carolina. *Environmental Science & Technology Letters*, 3:12:415. <https://doi.org/10.1021/acs.estlett.6b00398>.
- The Chemours Company, 2016. *NPDES Permit Renewal Application*, Wilmington, Del.
- USEPA (US Environmental Protection Agency), 2017a. *Assessing and Managing Chemicals Under TSCA: Risk Management for Per- and Polyfluoroalkyl Substances (PFASs) Under TSCA*. USEPA, Research Triangle Park, N.C. www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-and-polyfluoroalkyl-substances-pfass (accessed Dec. 18, 2017).
- USEPA, 2017b. *Method for Extraction and Analysis of Perfluoroethercarboxylic Acids (PFECAs) From Surface Water, Well Water and Waste Water by Ultra-Performance Liquid*

- Chromatography (UPLC)-Tandem Mass Spectrometry (MS/MS).* D-EMMD-PHCB-62-SOP-01. USEPA, Research Triangle Park, N.C.
- USEPA, 2017c. *Laboratory PFAS Results for NC DEQ Cape Fear River Water Sampling.* https://files.nc.gov/ncdeq/GenX/NC%20DEQ%20Report_4_Nontargeted.pdf (accessed Mar. 26, 2018).
- USEPA, 2016a. *Drinking Water Health Advisory for Perfluorooctane Sulfonate (PFOS) 822-R-16-004.* USEPA, Research Triangle Park, N.C.
- USEPA, 2016b. *Drinking Water Health Advisory for Perfluorooctanoic Acid (PFOA) 822-R-16-005.* USEPA, Research Triangle Park, N.C.
- USEPA, 2009a. *United States Environmental Protection Agency Office of Pollution Prevention and Toxics Regulation of New Chemical Substances Pending Development of Information.* USEPA, Research Triangle Park, N.C.
- USEPA, 2009b. *Sample Collection Protocol for PFCs in Surface and Well Water.* SOP No. EMAB-113-0, USEPA, Research Triangle Park, N.C.
- USEPA, 2006. *Fact Sheet: 2010/2015 PFOA Stewardship Program.* USEPA, Research Triangle Park, N.C.
- Vecitis, C.D.; Park, H.; Cheng, J.; Mader, B.T.; & Hoffmann, M.R., 2009. Treatment Technologies for Aqueous Perfluorooctanesulfonate (PFOS) and Perfluorooctanoate (PFOA). *Frontiers of Environmental Science & Engineering*, 3:2:129. <https://doi.org/10.1007/s11783-009-0022-7>.
- Wagner, A. & Buckland, T., 2017. Chemours: GenX Polluting the Cape Fear Since 1980. *Wilmington Star News*, June 15. www.starnewsonline.com/news/20170615/chemours-genx-polluting-cape-fear-since-1980 (accessed Dec. 18, 2017).
- Wang, Z.; DeWitt, J.C.; Higgins, C.P.; & Cousins, I.T., 2017. A Never-Ending Story of Per- and Polyfluoroalkyl Substances (PFASs)? *Environmental Science & Technology*, 51:5:2508. <https://doi.org/10.1021/acs.est.6b04806>.
- Wang, J.; Wang, X.; Sheng, N.; Zhou, X.; Cui, R.; Zhang, H.; & Dai, J., 2016. RNA-Sequencing Analysis Reveals the Hepatotoxic Mechanism of Perfluoroalkyl Alternatives, HFPO₂ and HFPO₄, Following Exposure in Mice. *Journal of Applied Toxicology*, 37:4: 436. <https://doi.org/10.1002/jat.3376>.
- Watanabe, N.; Takata, M.; Takemine, S.; & Yamamoto, K., 2018. Thermal Mineralization Behavior of PFOA, PFHxA, and PFOS During Reactivation of Granular Activated Carbon (GAC) in Nitrogen Atmosphere. *Environmental Science and Pollution Research*, 25:8:7200. <https://doi.org/10.1007/s11356-015-5353-2>.
- Watanabe, N.; Takemine, S.; Yamamoto, K.; Haga, Y.; & Takata, M., 2016. Residual Organic Fluorinated Compounds From Thermal Treatment of PFOA, PFHxA and PFOS Adsorbed Onto Granular Activated Carbon (GAC). *Journal of Material Cycles and Waste Management*, 18:4:625. <https://doi.org/10.1007/s10163-016-0532-x>.
- Woodard, S.; Berry, J.; & Newman, B., 2017. Ion Exchange Resin for PFAS Removal and Pilot Test Comparison to GAC. *Remediation: The Journal of Environmental Cleanup Costs, Technologies & Techniques*, 27:3:19.
- WV DEP (West Virginia Department of Environmental Protection), 2011. Consent Order No. 7418. WV DEP, Charleston, W.V.
- Xiao, X.; Ulrich, B.A.; Chen, B.; & Higgins, C.P., 2017. Sorption of Poly- and Perfluoroalkyl Substances (PFASs) Relevant to Aqueous Film-Forming Foam (AFFF)-Impacted Groundwater by Biochars and Activated Carbon. *Environmental Science & Technology*, 51:11: 6342. <https://doi.org/10.1021/acs.est.7b00970>.
- Zaggia, A.; Conte, L.; Falletti, L.; Fant, M.; & Chiorboli, A., 2016. Use of Strong Anion Exchange Resins for the Removal of Perfluoroalkylated Substances From Contaminated Drinking Water in Batch and Continuous Pilot Plants. *Water Research*, 91:137. <https://doi.org/10.1016/j.watres.2015.12.039>.